

THE OXIDATION OF CARBON MONOXIDE USING TIN OXIDE BASED CATALYSTS

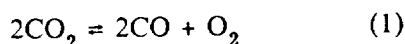
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SUMMARY

The preparation conditions for precious metal/tin oxide catalysts were optimised for maximum carbon monoxide/oxygen recombination efficiency. This was achieved by controlling the tin digestion, the peptisation to form the sol, the calcination process and the method of adding the precious metals. Extensive studies of the tin oxide structure were carried out over the temperature range 20 to 500°C in air or hydrogen environments using Raman scattering and X-ray diffraction. Adsorbed species on tin oxide, generated in an environment containing carbon monoxide, gave rise to a Raman band at about 1600 cm⁻¹ which was assigned to carbonaceous groups, possibly carbonate.

INTRODUCTION

Closed cycle CO₂ gas lasers are used in several applications. These applications can range from highly technical observation systems to heavy duty steel cutting tools. During the operation of these lasers dissociation of carbon dioxide occurs as shown in equation 1.



Molecular oxygen reduces the stability and operational efficiency of the laser; therefore, it is essential that the level is kept to a minimum. It is known that the recombination of CO and O₂ to form CO₂ can be achieved using a suitable catalyst (ref 1). The catalyst used in this application must meet the following requirements:-

1. The recombination of CO and O₂ at a rate at least equal to the generation rate.
2. It must be stable over a long time.
3. Under operational conditions it must maintain adequate efficiency.
4. The device must be mechanically stable during transportation, operation and non-working periods.

We have shown that high surface area tin oxide may be coated with various precious metals forming a catalyst with high activity for CO oxidation. However, the stability and efficiency of the final catalyst is crucially dependent on both the preparation conditions and the subsequent heat treatments.

The aims of the work reported here were to prepare a catalyst that would be effective under carbon dioxide laser conditions and to examine the effect of the preparation parameters on the structure and activity of these materials.

EXPERIMENTAL

Tin Oxide Sol Preparation

Tin (IV) oxide may be prepared directly from tin metal by controlled reaction with nitric acid. The dispersed oxide particles have a size which is dependent on the concentration of the acid, generally being larger for higher concentrations. The dried metastannic acid is non-crystalline, but crystallinity develops on calcining at 350°C.

The physical and chemical properties of commercial metastannic acid can be quite variable, perhaps due to differences in the preparation conditions. The tin oxide used in this work was therefore freshly prepared using Analar grade chemicals.

To form a tin oxide sol which can be used for coating substrates metastannic acid is peptised using an organic base. To do this the precipitated metastannic acid is thoroughly washed, removing ions, until the supernatant liquid has a conductivity of 4.5 mS or less. It will then peptise in the organic base, forming a sol with an oxide content typically 300g l⁻¹, with particles of average size 210 nm (measured using a Malvern Zetasizer). The tin oxide catalyst support is then obtained by drying and then calcining at 350°C.

Precious Metal Catalyst Preparation

Tin oxide prepared by the method described above was impregnated with precious metal by one of the two routes listed below:

- (a) Co-precipitation achieved by mixing the components at the sol stage, followed by drying and calcination.
- (b) Wet impregnation of the dried and calcined tin oxide, followed by drying and calcination (incipient wetness technique).

The precious metals Pt and Pd were added such that the content after calcination at 350°C was in the range 0 to 3% of the tin oxide mass.

Activity Testing

All the samples discussed in this paper were pretreated and activity tested under identical conditions. After the calcination treatment the sample was mounted in the test reactor, reduced in a H₂/He gas stream and finally stabilised in oxygen. The activity testing was carried out in a flowing gas mix of 0.5% O₂, 1.0% CO and 98.5% N₂ at a space velocity of 36000 h⁻¹, and the unreacted CO and O₂ monitored to determine the recombination rate for the catalyst.

Raman Spectroscopy

The Raman Scattering experiments were carried out using a Spex Triplematic monochromator fitted with an intensified 1024 photo-diode detector. The laser beam sources were capable of being adjusted over a wavelength range 441 nm (He/Cd) to 514 nm (Ar ion). The power of the source beam was 100 m watts but was reduced to 10 m watts at the sample. To obtain comparable results all the high temperature oxidising and reducing atmosphere experiments were carried out using a Stanton Redcroft HSM 5 Hot Stage.

X-Ray Diffraction

The room temperature X-ray diffraction experiments were carried out using a Siemens fully automated D500 X-ray Diffractometer with copper K_{α} radiation and analysed using a secondary monochromator through a scintillation counter.

The high temperature experiments were carried out using a Harwell designed precision apex goniometer with a G.T.P Engineering high temperature attachment. The specimen hot stage assembly is controlled by a Eurotherm micro processor system. The primary beam was Cu K_{α} radiation and the diffracted beam passed through a curved graphite crystal secondary monochromator. Data collection was carried out using a Hewlett-Packard series 200, 9816 micro-computer.

RESULTS AND DISCUSSION

Activity Testing

Powdered catalysts prepared by the incipient wetness technique were more active than those containing the same quantity of precious metals prepared by the co-precipitation route. This is possibly due to a proportion of the precious metals being locked inside the tin oxide particles and hence unavailable for reaction. All subsequent experiments were conducted using catalysts prepared by the incipient wetness technique.

Mixtures containing 0, 1, 2 or 3% Pt and Pd were prepared as indicated in Table 1. Each of these powdered mixtures was tested for oxygen removal activity at room temperature over a period of about 40 min. The activity measurements, shown in figures 1, 2 and 3, suggest that the Pt/Pd samples fall into three categories. The first group contained the 2% Pd, 2% Pt, 1% Pt/1% Pd, and 1% Pt/2% Pd samples. Each of these activated to some extent, especially the 2% Pt sample, but then deactivated later in the test (figure 1). Despite this deactivation, the 2% Pt sample was more active at the end of the test than those in the second group.

This second group, containing the 3% Pt/1% Pd, 2% Pt/1% Pd and 1% Pt/3% Pd samples sustained activity at a reasonable level for the duration of the test (figure 2). The third group containing the 2% Pt/2% Pd, 2% Pt/3% Pd, 3% Pt/2% Pd and 3% Pt/3% Pd samples continued activating during the test period (figure 3).

The final level of activity of the Pt/Pd samples containing 2 or 3% Pt was similar in each case, except for the 2% Pt/2% Pd and was in excess of 90%. It was therefore difficult to further analyse these results, but for the samples with lower precious metal concentrations this was possible. The sample containing 2% Pt was more than twice as active as that containing 2% Pd. Also from the activity profiles for 1% Pt/Pd samples it can be seen that 3% Pd (ie. 1% Pt/3% Pd) gives activity similar to, but still less, than for the 2% Pt sample.

Catalytic activity was increased by adding more Pt or Pd, but was more critically dependent on the Pt content. Because the catalysts were operating in excess of 90% conversion in many cases the apparent effect of increasing precious metal loading was to sustain the high level of activity for a longer period of time. This has also been observed for powdered or coated monolith catalysts tested at 60°C, where activity is sustained for longer periods of time.

Effect of Calcination on Tin Oxide Structure

The X-ray diffraction profile for metastannic acid calcined at 350°C has very broad peaks indicating poor crystallinity, which was only marginally improved on calcining at 600°C. On calcining at 1000°C the peaks sharpen considerably. It was only possible to obtain a Raman spectrum with well defined peaks for the 1000°C calcined sample.

A sample of un-peptised tin oxide was then enclosed in a cell and heated at intervals of 100°C from room temperature to 500°C. The sample was heated for 30 min at each set temperature prior to the Raman spectrum being recorded. It can be seen from the spectra in figure 4 that the A_{1g} band moved from 635 cm^{-1} at 20°C to 626 cm^{-1} at 500°C, and that the B_{2g} band originally at 776 cm^{-1} moved similarly. The temperature dependence of the wavenumber shift is displayed in figure 5. The spectra observed are very similar in appearance to those recorded previously for single crystals (ref 2) and textured samples (ref 3), and the wavenumber shift mimics that observed for single crystals (ref 4).

On expanding the spectra in figure 4 it was noted that the E_g band at 477 cm^{-1} decreased in intensity with increasing temperature while the band at 502 cm^{-1} increased. Several other bands, notably those around 240 and 540 cm^{-1} , became more resolved as the temperature increased. This could be due to orientation effects of small crystallites occurring in the random powder sample. These changes have been observed for many samples and appear characteristic of the tin oxide.

An identical series of experiments was carried out for base peptised tin oxide, with very similar results to those for the un-peptised material.

The lattice parameters were calculated from X-ray spectra collected at each temperature. From these results the coefficient of expansion has been calculated to be $a = 6.10 \times 10^{-6}$ per °C and $c = 6.28 \times 10^{-6}$ per °C.

Tin Oxide Reduction

It has been observed that tin oxide/precious metal catalysts have enhanced activity if treated in a reducing atmosphere prior to use. In this series of experiments tin oxide was subjected to hydrogen/helium atmospheres over the temperature range 20 to 500°C. Using Raman and X-ray techniques it was hoped that any changes in the oxidation state of the tin would be observed.

The cell was well flushed with H_2/He prior to heating the sample in exactly the same fashion as for the calcinations. The spectrum recorded at 20°C had a much higher background than that in air, but the A_{1g} and B_{2g} bands were clearly visible (figure 6). As the temperature increased so did the background intensity. This may be due to changes either in the hydroxyl groups or the electronic nature of surface lattice sites. Local electronic changes can cause band fluorescence producing a rise in the background intensity. A study was made in the region about 3600 cm^{-1} for surface hydroxyl groups, but none were detected.

Since the Raman spectra revealed no reduced tin it was decided to repeat the experiments using X-ray diffraction instead. The representative sample of the resulting X-ray profiles displayed in figure 7 shows there was no phase transition or partial reduction from Sn^{4+} to Sn^{2+} , but there was a change in the lattice spacing of the tin oxide. After cooling the sample to 20°C in the H_2/He gas flow, spectra indicated that a small quantity of β -tin was present in the dominant SnO_2 phase. It is surprising that heterogeneous oxide phases were not observed when the sample was being heated to 500°C.

Geurts et al (ref 3) observed a partial phase change when heating SnO in air below 450°C with both SnO_2 and β -tin present. On continuing heating to 650°C the SnO and β -tin were completely transformed to SnO_2 .

Peptised Tin Oxide in a CO Environment

Experiments were conducted in the high temperature Raman cell in order to determine the influence of carbon monoxide, present at 5% of an otherwise helium flow, on the reduction of the tin oxide. Just below 200°C a band developed at approximately 1600 cm^{-1} . On heating further towards 500°C the band intensified (figure 8), and persisted on cooling to 20°C.

This band can be attributed to the CO stretch in, for example, a carbonate formed on the surface of tin oxide. Such bands have also been observed for silica and alumina samples in similar environments and conditions (ref 5).

Precious Metal/Tin Oxide Catalysts

A precious metal coated tin oxide sample was calcined at 1000°C for 1h in air. On cooling to 20°C the Raman spectrum contained the A_{1g} and B_{2g} bands with a high background. This high background is a common feature of precious metal coated oxides, eg. alumina, and is due to the limited penetration of the laser system.

On heating the sample in a CO/He environment a small band appeared at about 1600 cm^{-1} at 100°C , a considerably lower temperature than for the tin oxide. As for the tin oxide sample, this band grew with increasing temperature up to 500°C . However, the species disappeared on cooling to 20°C , probably due to desorption or catalytic decomposition under the influence of the precious metal.

This influence of precious metals, or indeed transition metals, on the presence of adsorbed species on support oxide surfaces is commonly observed. An example is the formation of species such as NCO from CO and NO on the metal, followed by migration onto the support. The catalytic reaction forming NCO can occur directly on the oxide surface, but at a significantly higher temperature.

CONCLUSIONS

To achieve optimum catalyst performance the preparation of the metastannic acid and peptisation to form the tin sol must be carefully controlled. If the tin oxide is calcined at 350°C a stable, high surface area support is obtained. Greater crystallinity can be induced by heating to 1000°C , but this is accompanied by a decrease in surface area. The precious metals were then best added subsequently by the incipient wetness technique. It was noted that 2% Pt on tin oxide had an activity several times that for a 2% Pd catalyst, and that the higher Pt/Pd loaded catalysts had extended lifetimes.

Some temperature dependent structural changes were observed using Raman and X-ray techniques for tin oxide when heated in air or hydrogen environments, however no reduction of Sn^{4+} was observed. On cooling from 500°C to 20°C in H_2/He some β -tin was produced. Data collected in this environment suggested that the quantity of surface hydroxyl groups was very low.

Species formed on tin oxide in He/5% CO above 200°C gave rise to a band at about 1600 cm^{-1} . The band persisted on cooling to 20°C , and is assigned to the CO stretch, possibly in a carbonate. In the presence of precious metal the band appeared at about 100°C , but disappeared on cooling from 500 to 20°C . This was attributed to the catalytic effect of the precious metal.

ACKNOWLEDGEMENTS

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Table 1. Precious metal tin oxide catalysts

Pd (w/o)	Pt loading 0 w/o	Pt loading 1 w/o	Pt loading 2 w/o	Pt loading 3 w/o
0			x	
1		x	x	x
2	x	x	x	x
3		x	x	x

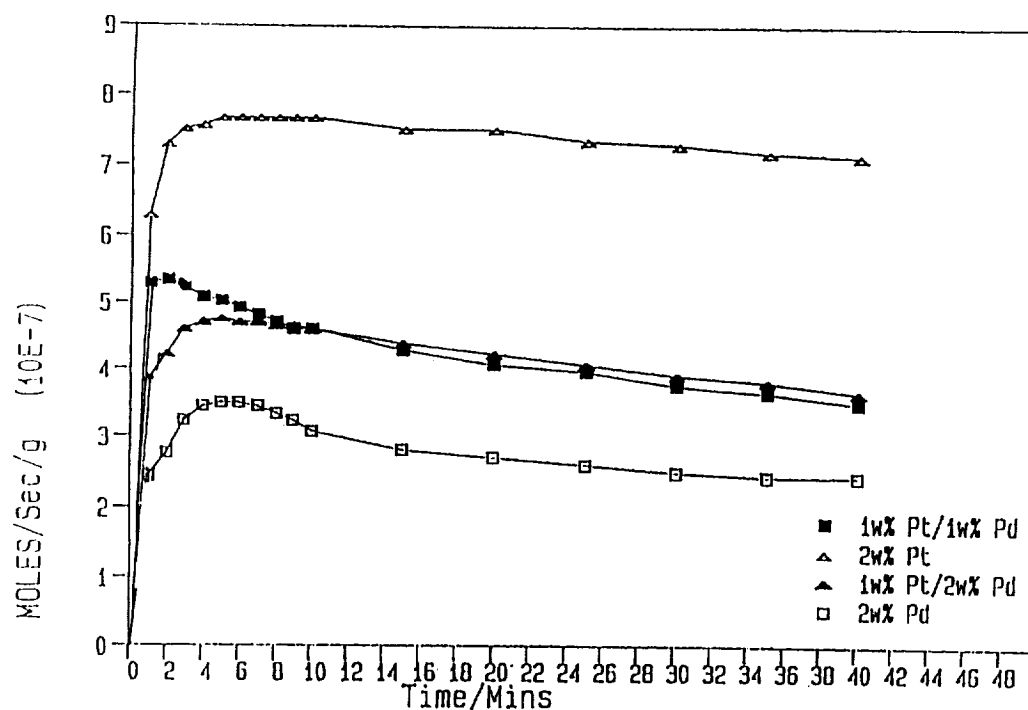


Figure 1. Activity tests of group 1 catalysts.

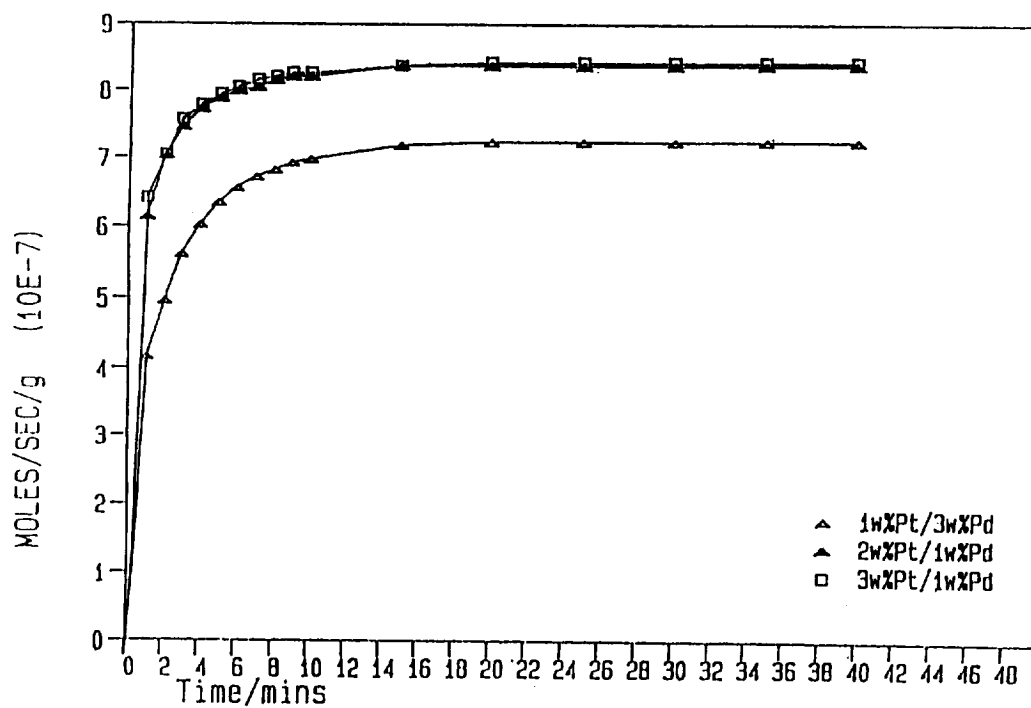


Figure 2. Activity tests of group 2 catalysts.

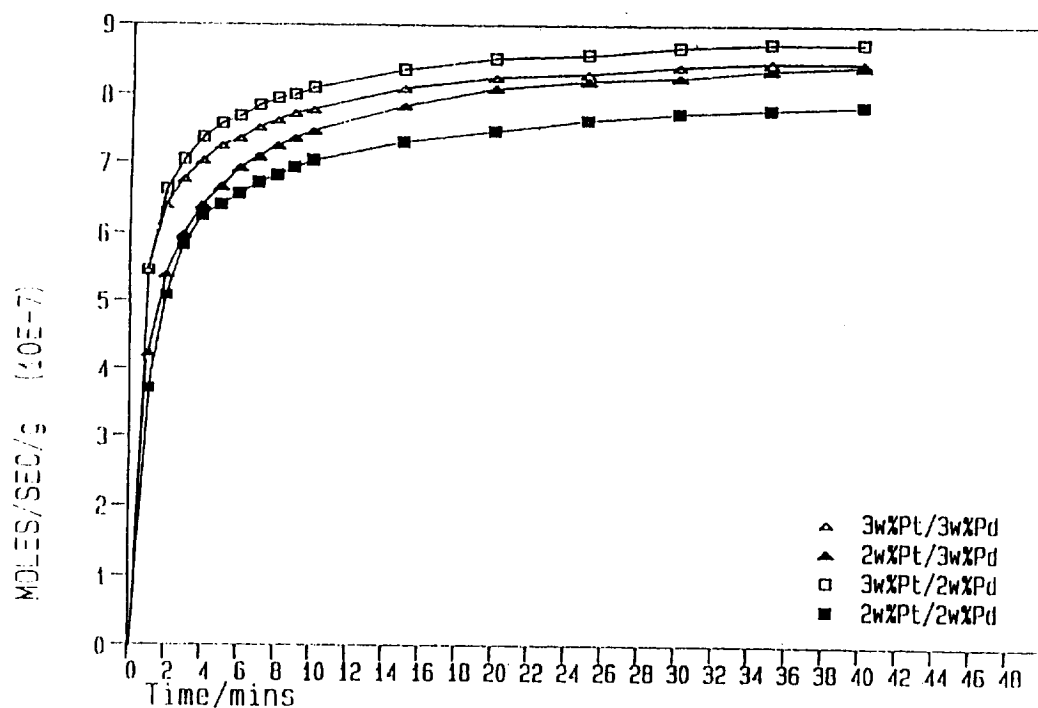


Figure 3. Activity tests of group 3 catalysts.

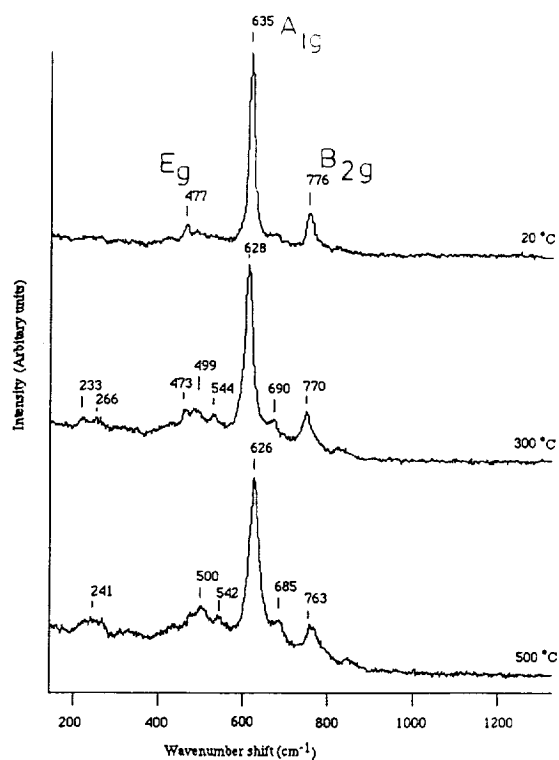


Figure 4. High-temperature Raman spectra of SnO_2 in air.

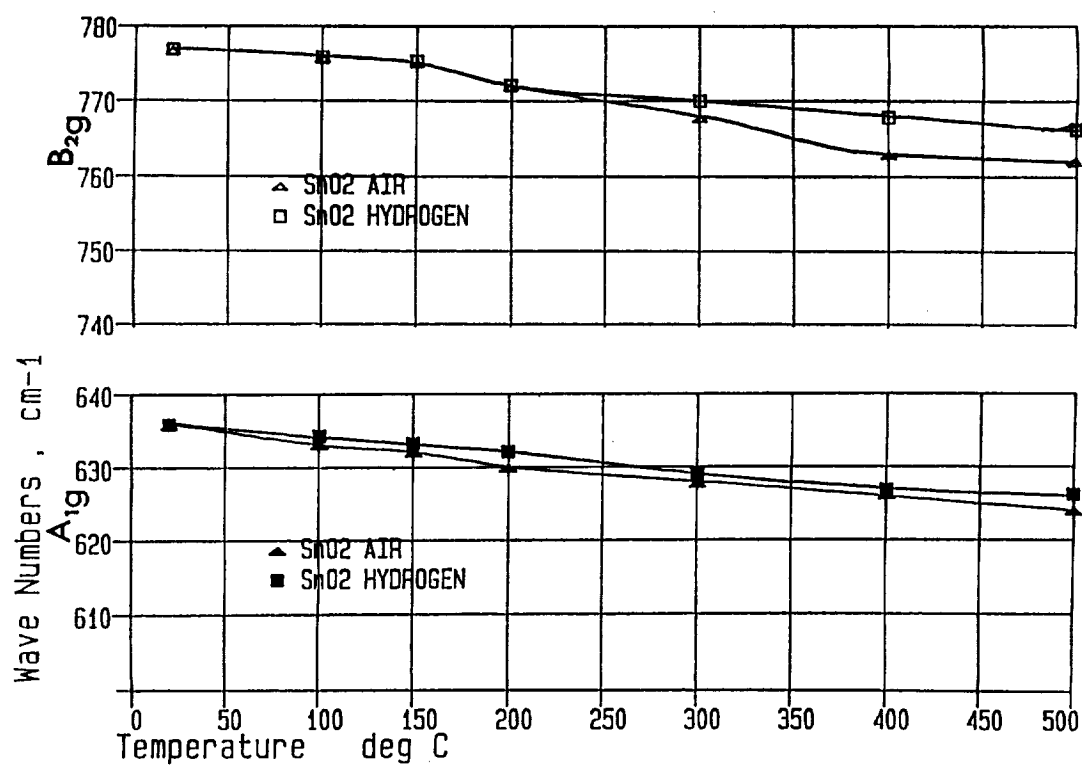


Figure 5. Temperature dependence of frequencies of Raman-active modes in SnO_2 .

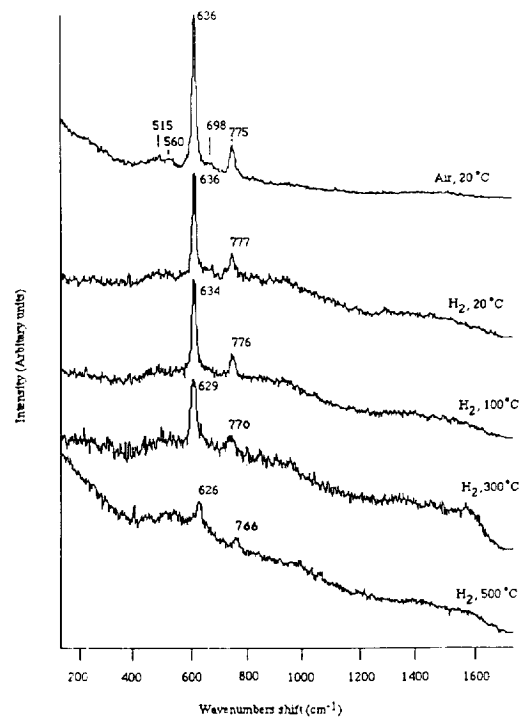


Figure 6. High-temperature Raman spectra of peptised SnO_2 in hydrogen.

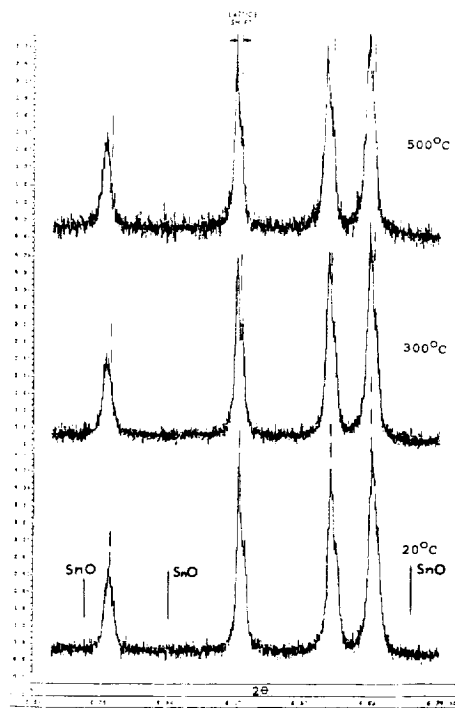


Figure 7. High-temperature X-ray diffraction pattern for SnO_2 in hydrogen gas mix.

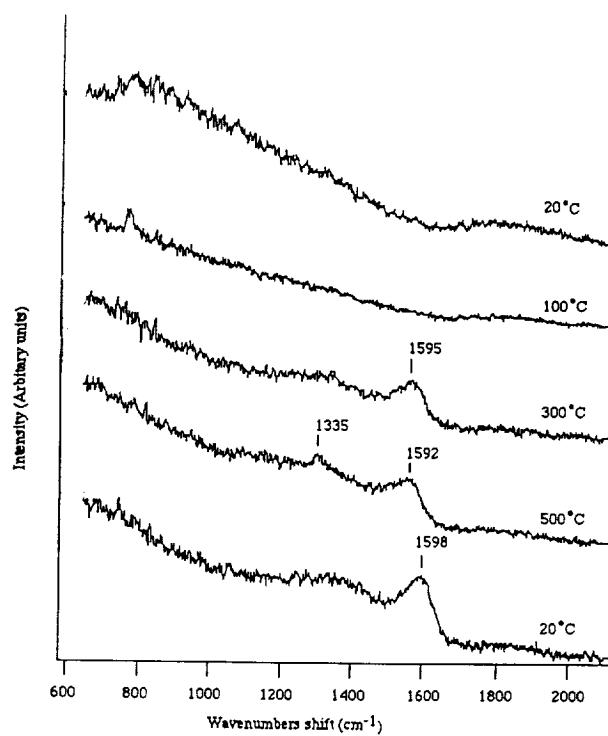


Figure 8. High-temperature Raman spectra of SnO_2 in CO .